

## AMPHOTERIC REACTIONS OF SUPERCRITICAL WATER WITH COAL MODELS

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### INTRODUCTION

For the past several years this laboratory has been studying water assisted coal liquefaction. Initial experiments were designed to determine whether water could replace all or part of the donor solvent in coal liquefaction [1]. More recent work has focused upon the chemical reactions of coal models in supercritical water [2].

In summary of our experiments with coal [1], high conversions of Illinois No. 6 (River King Mine) bituminous coal were obtained in minireactor experiments at modest temperatures with little or no hydrogen-donor solvents.

The use of water in liquefaction has also been studied by others. When used in combination with carbon monoxide and a suitable catalyst, water was a source of hydrogen for the reduction of coal [3,4]. Liquefaction under carbon monoxide, without an organic solvent, has also been carried out with slurries composed of coal and either water or aqueous base [5,6]. In some cases, water served to carry dissolved metal salts used as homogeneous catalysts as well as acting as the liquefaction medium [7]. In comparison with conventional organic liquefaction solvents, water is quite effective when used in combination with H<sub>2</sub>S, in particular under synthesis gas rather than hydrogen [8]. Aqueous liquefaction using impregnated catalysts has also been combined with supercritical water distillation to separate the oil and asphaltene from the coal char residue [9]. The simple treatment of coal with supercritical water in the absence of hydrogen or catalysts renders a substantial portion of the treated coal extractable by tetrahydrofuran [10]. From these extraction studies, it is apparent that water is able to assist the diffusion and dispersion of liquefaction products and reactants.

In addition to these roles, water may directly participate as a reactant in the thermolytic chemistry of certain model compounds. In the presence of water, dibenzyl ether decomposes at 374°C by both pyrolytic and hydrolytic pathways [11]. The removal of nitrogen from heterocyclic compounds, such as isoquinoline, is accelerated in the presence of supercritical water [12]. Most recently, it was suggested

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that in the presence of supercritical water the hydrolysis of coal models proceeds through a transition state that is more polar than the reactants [13].

Taken together, these studies indicate that under various conditions, supercritical water may act as a good liquefaction medium, dissolve or extract coal-derived liquid products, promote the cleavage of certain bonds likely to be found in coal, provide hydrogen through the water-gas shift reaction, and possibly assist the contacting of coal with catalysts or hydrogen.

For the past year our efforts have centered upon the study of two distinct coal model compound systems with water under liquefaction conditions. This research is intended to further evaluate the chemical role of water above its critical temperature in the conversion of coal to a liquefaction product.

## EXPERIMENTAL

Commercially available reagents were used without further purification. Bibenzyl (Aldrich), benzyl phenyl ether (TCI), and hydroquinone monobenzyl ether (Fluka) were analyzed for purity by gc/ms prior to use. All other models were synthesized from the commercially available substituted benzyl halides, with the exception of 2-bromo-p-toluic acetate which was synthesized from the reaction of diazomethane with 2-bromo-p-toluic acid. Reaction of the benzyl halides with triethylphosphite afforded the phosphonates which were in turn coupled via Wittig reaction with benzaldehyde or benzyl-ether-protected salicylaldehyde to form the substituted stilbenes and protected o-hydroxystilbenes respectively. Hydrogenation of the stilbenes over Pd/C afforded the desired products.

A five minireactor system [14] at the Pittsburgh Energy Technology Center was employed for all reactions with the bibenzyls. The bibenzyls (2.6 mmol) were reacted in the presence of 4.3 mL H<sub>2</sub>O and/or D<sub>2</sub>O solutions containing 2 mL n-pentanol as an internal standard per 93.4 mL H<sub>2</sub>O or 100 mL D<sub>2</sub>O. The reactors were purged with N<sub>2</sub> then submerged into a fluidized sand bath at 400 °C for 3 hours. The pressure of the reactants was not measured directly; using van der Waal's equation the partial pressure of water was estimated at 4290 psi. The density of the supercritical water was 0.10 g/mL. Once cooled, the reactors were washed several times with 5 mL dichloromethane. The resulting heterogeneous solutions were agitated for several days. Each organic layer was analyzed on DB1 capillary column using an HP #5790A gc and a HP #5970A MSD.

In the study of the benzyl phenyl ethers, 0.5 mmol of each model was reacted with 2.9 mL  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  (0.16 mmol) at  $400^\circ\text{C}$  for forty minutes using a Parr # 4704 22 cc minireactor. The estimated pressure and water density in these reactions was 5900 psi and 0.13 g/cc. An internal standard was not employed in these studies and molecular oxygen was not excluded. Analysis was identical to that described above with the substitution of ether for  $\text{CH}_2\text{Cl}_2$ .

## DISCUSSION

In the first study, a Hammett series of substituted bibenzyls and o-hydroxy bibenzyls were synthesized via Wittig reaction with subsequent hydrogenation. The substituents synthesized were p- $\text{NH}_2$ , p-t-Bu, p- $\text{CH}_3$ , H, m- $\text{CF}_3$ , and p- $\text{CH}_3\text{O}_2\text{C}$ .

Not surprisingly, thermolysis pathways dominated the observed products from these preliminary reactions of the substituted bibenzyls. Both the thermolysis products and recovered starting materials were observed to undergo deuterium exchange. The major products from all reactions with the bibenzyls and o-hydroxybibenzyls, along with the maximum number of deuterium incorporated into each, are compiled in Table 1.

With the simple bibenzyls, electron donating substituents were observed to enhance D-substitution into the recovered starting materials. D-exchange may be envisioned by either radical or ionic pathways as illustrated in Scheme 1. Ionic route B would be stabilized by electron donating groups, but alcohol products would be expected and these have not been observed. Ionic route C forms carbanion intermediates, hence electron withdrawing groups would be expected to stabilize the intermediates. Electrophilic aromatic substitution, illustrated via route A, would agree with the observed substituent effects, since electron donating groups would be expected to stabilize the intermediate arenium ions.

In the case of p-carboxylic acid methyl ester bibenzyl, demethylation and decarboxylation predominated with a deuterium substitution pattern suggestive of an ionic decarboxylation.

Comparison of the conversions of the o-hydroxy substituted bibenzyls in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  suggested a primary isotope effect. This is an intriguing observation considering that thermolysis pathways again predominated.

The o-hydroxy bibenzyls exhibited more extensive deuterium exchange than with the simple bibenzyls, presumably due to the enhanced H(D)-atom transfer ability of the phenolic-H(D). The tautomerization pathway [15] contributed significantly to the product distribution with the o-hydroxy bibenzyls. The production of substituted ethylbenzenes also exhibited a

primary isotope effect suggesting that tautomerization is rate limiting.

2-Ethyl-4-substituted biphenyl ethers were also observed in some cases, presumably through the rearrangement of the respective substituted o-hydroxybibenzyls (Scheme 2.).

Cyclization of p-NH<sub>2</sub>-, p-CH<sub>3</sub>-, and H- o-hydroxy substituted bibenzyls to dibenz[b,f]dihydrooxepane was also observed. Two possible mechanisms for these transformations are illustrated in Scheme 3.

In our other preliminary study, benzyl phenyl ether (BPE) reactions pathways were complicated by the presence of molecular oxygen. For example, in addition to the thermolysis products phenol and toluene, autooxidation product benzaldehyde was also observed. Significant amounts of benzylalcohol and o-benzyl phenol were also produced. Both products can be explained through ionic reactions with water, although the former may also result from autooxidation.

Hydroquinone monobenzyl ether (HQMBE) also exhibited the expected thermolysis products hydroquinone and toluene, as well as the autooxidation product benzaldehyde. The tautomeric pathway was also important as evidenced by the significant production of benzylalcohol. The observed formation of catechol monobenzyl ether (CMBE) may also be simply explained by the recombination of phenoxy and benzoxy radicals, both requiring tautomerization for their generation. The deuterium substitution pattern of CMBE, however, suggests a fascinating mechanistic alternative. CMBE from reaction in D<sub>2</sub>O exhibited its parent ion at 203 m/e, an increase of three from unsubstituted CMBE. Recovered HQMBE exhibited its parent at 201 m/e, indicating only one deuterium substitution. If the methylene protons were responsible for the additional exchange in CMBE, similar D-substitution patterns would be expected for both HQMBE and CMBE.

Two successive nucleophilic aromatic substitutions of D<sub>2</sub>O with HQMBE would account for the observed substitution pattern. The first substitution would give resorcinol monobenzyl ether, followed by a more facile second to yield the thermodynamically preferred CMBE. This possibility is illustrated in Scheme 4.

The impact of these preliminary model compound studies toward an understanding of the organic chemical reactions of coal in supercritical water is striking. The observation that electron donating substituents favored D-exchange with the substituted bibenzyls supports our earlier suggestion [2] that electrophilic aromatic substitution by a proton for suitable aryl substituents is a possible alternative reaction pathway for coal in the presence of water. Even more dramatic is the possibility of nucleophilic aromatic substitution with water as suggested by the production and D-substitution pattern of CMBE. Such a reaction would be

consistent with the observed production of phenols during liquefaction.

The heterogeneous nature of coal requires that we view liquefaction as mechanistically complex. The results of this preliminary study suggest that the unique amphoteric character of water may present coal with reaction pathways unavailable under traditional liquefaction conditions.

## ACKNOWLEDGMENTS

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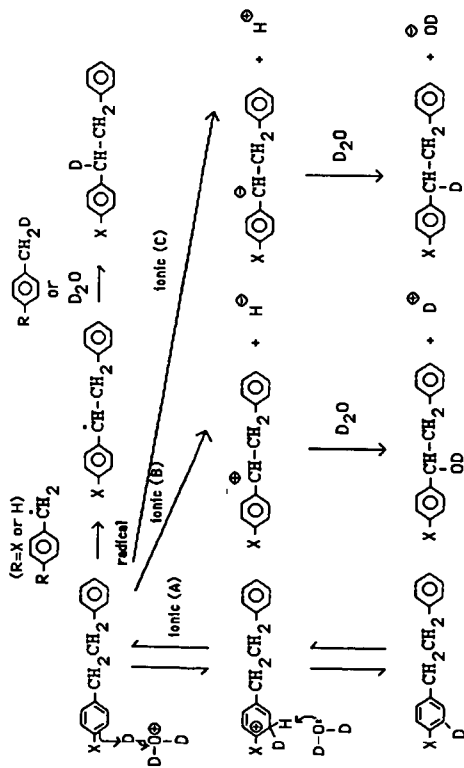


Table 1. Major Products from the Reaction of Supercritical Water with

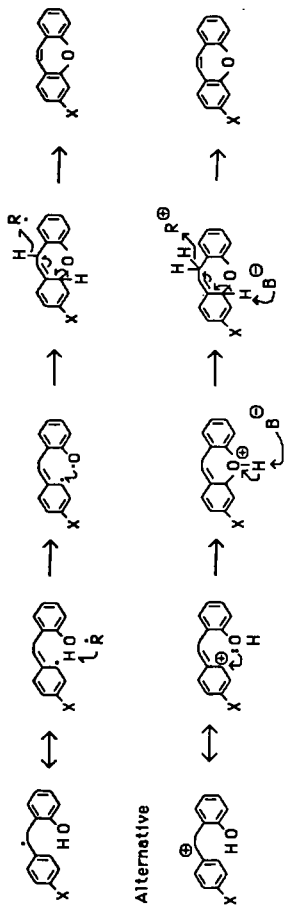
X	products	OH		X-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>		C <sub>6</sub> H <sub>4</sub> -CH <sub>3</sub>		X-C <sub>6</sub> H <sub>4</sub> -CH <sub>3</sub>		starting materials		rearranged compound		epicis compound		High m. wt. compounds	
		OH	H	OH	H	OH	H	OH	H	OH	H	OH	H	OH	H	OH	H
NH <sub>2</sub>	H <sub>2</sub> O	0.22 <sup>(1)</sup>	-	0.16	-	0.56	-	0.062	-	0.84	-	Y	-	OB	-	OB	-
	D <sub>2</sub> O	ND	ND	ND	ND	ND	0.21 <sup>3D</sup>	ND	0.12 <sup>6D</sup>	-	1.44 <sup>5D</sup>	ND	ND	OB	ND	OB	ND
CH <sub>3</sub>	H <sub>2</sub> O	0.12	-	0.15	-	0.27	-	0.36	-	0.80	-	OB	-	OB	-	OB	-
	D <sub>2</sub> O	ND	ND	ND	ND	trace	-	0.053 <sup>3D</sup>	-	1.85 <sup>6D</sup>	-	DB	ND	OB	ND	OB	-
H	H <sub>2</sub> O	0.009	-	0.08	-	0.10	-	0.32	-	1.01	-	OB	-	OB	-	ND	-
	D <sub>2</sub> O	0.062 <sup>3D</sup>	ND	0.026 <sup>4D</sup>	ND	0.23 <sup>6D</sup>	0.13 <sup>2D</sup>	0.15 <sup>3D</sup>	0.13 <sup>2D</sup>	1.51 <sup>7D</sup>	2.39 <sup>3D</sup>	OB	ND	OB	OB	ND	trace
m-CF <sub>3</sub>	H <sub>2</sub> O	ND	-	0.017	-	0.014	-	0.10	-	1.14	-	OB	-	ND	-	OB	-
	D <sub>2</sub> O	ND	ND	ND	ND	0.069 <sup>6D</sup>	0.16 <sup>2D</sup>	0.053 <sup>3D</sup>	0.064 <sup>2D</sup>	1.34 <sup>3D</sup>	1.83 <sup>2D</sup>	OB	ND	ND	ND	OB	OB
CH <sub>3</sub> O <sub>2</sub> C	H <sub>2</sub> O	ND	-	ND	-	0.13	-	0.083 <sup>3D</sup>	-	-	-	ND	-	ND	-	OB	-
	D <sub>2</sub> O	ND	ND	ND	ND	0.047 <sup>6D</sup>	0.18 <sup>3D</sup>	0.069 <sup>5D</sup>	0.14 <sup>3D</sup>	0.021 <sup>3D</sup>	0.13 <sup>1D</sup>	ND	ND	ND	ND	OB	ND

(1) The numbers are the ratios of pentanol/product, measured by the area under the GC peaks. ND: not detected. number D: the number of possible deuteriums incorporated. OB: observed. (2) experimental value x 1/2

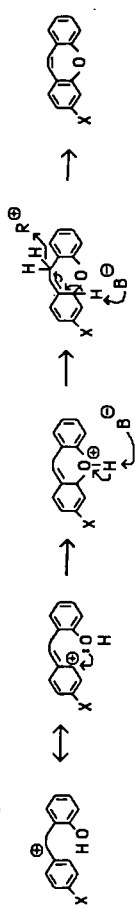
### Schema 1



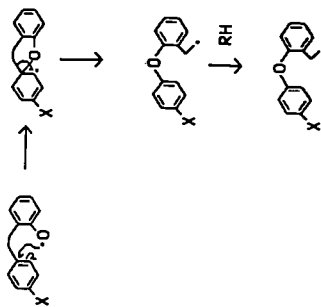
### Scheme 3



Alternative



### Scheme 2



**Table 2. Products from the Reaction of Supercritical Water with Benzyl Phenyl Ether and Hydroquinone Monobenzyl Ether<sup>1</sup>**

From Benzyl Phenyl Ether

recovered BPE  
phenol  
benzaldehyde  
benzylalcohol  
o- or p- benzyl phenol  
toluene

From Hydroquinone Monobenzyl Ether

recovered HQMBE  
catechol monobenzyl ether  
benzylalcohol  
p-cresol  
benzaldehyde  
toluene

<sup>1</sup> Products are listed in the order of abundance as estimated from gc/ms. Quantitative experiments are in progress with these models.

**Scheme 4. Suggested Mechanism for the Formation of Catechol Monobenzyl Ether**

